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Growth of Single Crystals and Fabrication of GaN and AlN Wafers

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13. ABSTRACT *(Maximum 200 words)*
GaN and AlN single crystals were grown from the vapor phase by evaporation of gallium or aluminum metals under an ammonia or nitrogen flow in a high temperature reactor. A growth rate of 500 µm/hr in the c direction was achieved for GaN while the growth rates for AlN were as high as a few millimeters per hour. The crystal size reached 3 mm for GaN and up to 15 mm for AlN. For both materials, the crystal aspect ratio (c/a) could be controlled by temperature and partial pressure of reactants. The resulting crystals were transparent and of excellent crystalline quality, as confirmed by x-ray diffraction, Raman scattering, and transmission electron microscopy studies. Photoluminescence studies on GaN conducted at 77 K showed a sharp emission peak centered at 359 nm. Time dependent photoluminescence measurements revealed optical metastability in bulk GaN.

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Growth of AlN Bulk Crystals from the Vapor Phase

Introduction

The objective of this project is the growth of high-quality AlN bulk crystals from the vapor phase. The equipment used for this purpose has been described previously. We continued exploring the parameter space of the growth system and have established two sets of growth parameters for Al and AlN source materials. We continued investigating seeded growth, and have improved reproducibility of results. A major update of our process monitoring and controlling software has been successfully implemented.

Experimental details

In the past quarter we focussed on the following experiments:

- A sequence of growth experiments from AlN source material was carried out at varying nitrogen pressures, all other relevant parameters remaining constant;
- Seeded growth was optimized; smaller AlN crystals grown in earlier experiments by spontaneous nucleation were used as seeds; reproducibility and temperature control issues were addressed in this context;
- Larger, and thicker c-oriented plates were grown and XRD studies were performed on these crystals.

All of the aforementioned experiments were carried out without any major hardware modifications of the growth system.

In view of improved process control and safety, the monitoring and controlling software was updated. Major safety improvements were implemented in order to enable longer, partially unattended growth experiments. Due to the high growth temperatures (typically 2300 C), redundant hardware and software interlocks were installed to monitor critical proces parameters, i.e., cooling water flow and temperature, total chamber pressure, electrical resistance of the heater element, and temperature of the heater (measured by pyrometer).

Overflow/underflow levels of the mentioned process variables are set by the software; if any of the process variables is found to be out of range the heater power is ramped down to leave the sytem in a safe standby mode. All of the safety interlocks were successfully tested.

Improved temperature stability over long growth runs (typically 24 hours) was achieved by implementing a constant-power algorithm that actively corrects the power supply current settings for changes in the heater element resistance. For safety reasons pyrometer temperature data are used for monitoring purposes only, while a power feed-forward algorithm controls the growth temperature. This approach yielded temperature drift better than 5C/24hrs at 2300C, which has been found to be sufficiently stable to guarantee reproducible growth results at this point.

Extensive data logging capabilities have been implemented as well, primarily in view of improved growth run documentation and failure analysis.

Experimental results

Nitrogen pressure: Growth experiments from AlN source material were carried out at nitrogen pressures in a range of 125 – 700 Torr. In this range the following observations were made:

- Mass transport from the AlN source to the cap of the crucible increased considerably with decreasing nitrogen pressure;
- Lower pressures yielded considerably thinner "a"-plates preferentially growing in their "c" direction; at higher pressures spontaneous nucleation yielded platelets with less extreme aspect ratios. Surface striations along the crystallographic "c" axis were primarily obeserved at higher pressures.

Seeded growth: Seeded growth results similar to those first reported in the previous quarterly report could be reproduced. High-temperature growth on the "c" faces of the seed crystals showed considerable anisotropy in growth speed depending on the polarity of the "c" faces. At this point we believe that the Al-terminated surfaces yield faster growth rates. In several instances we observed irregular growth on the "c" faces of seed crystals, which we attributed to partial oxidation of the Al-terminated face; annealing of the seed crystals in a nitrogen atmosphere at elevated temperature (2300 C) prior to the growth appears to circumvent this problem. More detailed studies are planned to address these issues.

XRD analysis of "c" plates: Several, approximately 1 mm thick AlN single crystals were grown from AlN source material, see Figure 1.

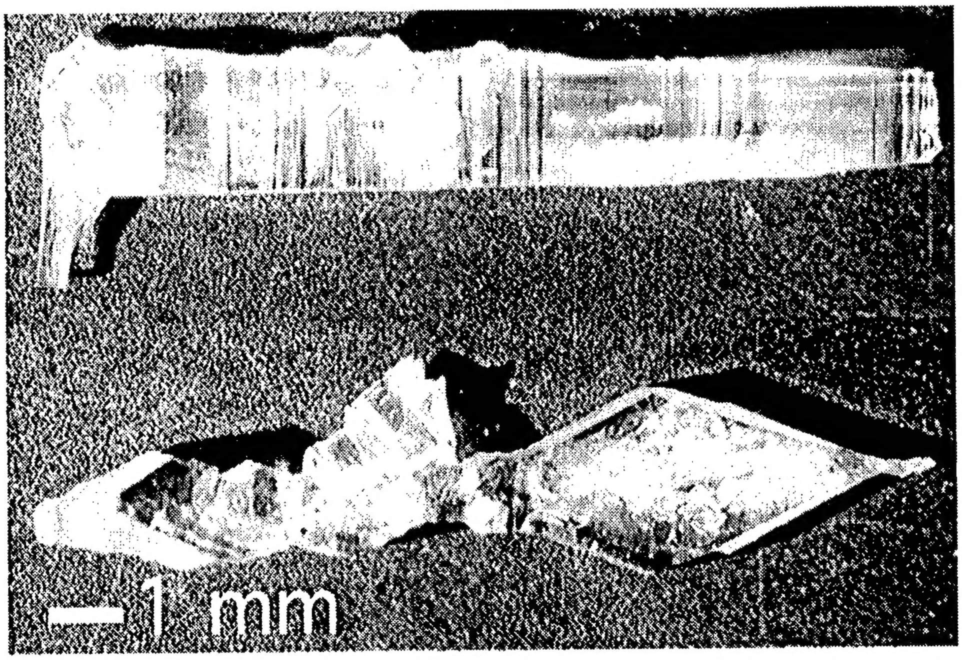

Fig.1: AlN crystal grown from AlN source material at elevated temperature (2300 C). Crystallographic c-axis is oriented along striations (top); largest surface is perpendicular to c-axis (bottom).

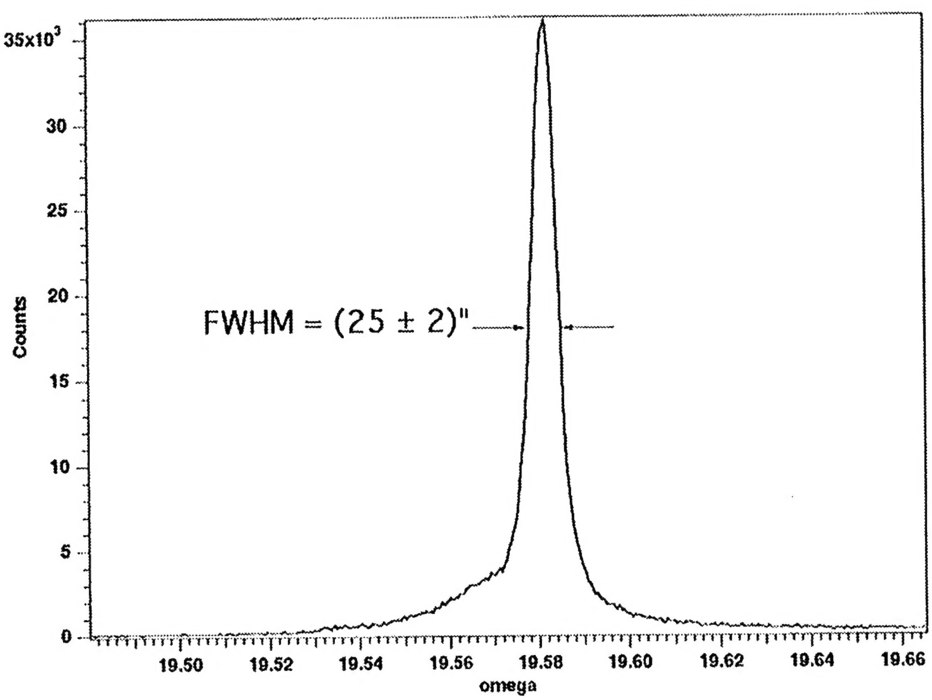

Fig.2: XRC (X-ray Rocking Curve) of the crystal shown in Fig. 1. XRC FWHM of (002) reflection was extremely narrow in the order of 25 arcsec.

Largest faces of the grown plates were perpendicular to the crystallographic c-axis. X-ray Rocking curves of the (002) reflection from these faces were extremely narrow, see Figure 2, thus indicating perfect crystallinity of these AlN single crystals. Rocking curves were taken from various areas of the crystal shown in Fig.1, and their respective FWHMs were in the order of 25 – 40 arcsec.

Conclusion

In the past quarter further systematic studies narrowed down the optimum parameters for the growth from Al and AlN source materials. Software updates and hardware safety additions have made the growth system sufficiently reliable to routinely perform partially unattended growth runs of 24+ hours duration. Seeded growth results are encouraging. High-temperature growth runs using AlN as source material have yielded single crystals of highest crystallinity, featuring very sharp XRC peaks.

Growth and Characterization of GaN Bulk Crystals

Abstract

Free-standing single crystals of bulk GaN were grown via unseeded vapor phase transport at 1130°C on hexagonal BN surfaces via direct reaction of Ga with ammonia. The number of nucleation events was reduced and the crystal size increased by introducing the ammonia at high temperatures. The resulting crystals were either needles or platelets depending on the process variables employed. Low V/III ratios achieved via ammonia flow rates $\leq$ 75sccm and/or ammonia total pressures $\leq$ 430Torr favored lateral growth. The average lateral growth rate for the platelets was ~50_m/hr; the average vertical growth rate for the needles was ~500_m/hr. Growth rates in all other directions for each of these two morphologies were very low. Seeded growth of both needle and platelet crystals was also achieved; however, the growth rate decreased at longer times and higher pressures due to reaction with H_2 from the increased decomposition of ammonia. Nitrogen dilution suppressed this decomposition. A 2mm x 1.5mm GaN crystal was grown with minimal decomposition in a 66.7%NH_3 and 33.3%N_2 gas mixture.

Introduction

Bulk GaN crystals have been produced by high pressure-high temperature solution growth[1], hydride vapor phase epitaxy[2], sublimation growth[3], flux growth[4], and vapor phase transport(VPT)[5]. The characteristics of the VPT technique include high growth rate(>500_m/hr), good aspect ratio control, a continuous supply of Ga and low production costs. However, there are difficulties inherent in this technique that must be surmounted to achieve the growth of crystals and boules of GaN of reasonable size and perfection.

Numerous nucleation events and the resulting formation of many small crystals have been major problems in growth via direct reaction of Ga vapor with ammonia[6]. To obtain macroscopic crystals, nucleation during the temperature ramp-up must be avoided. Aspect ratio control is another critical issue in bulk growth. It has been suggested[5,6] that a higher Ga flux promotes lateral growth; however, no systematic investigation has been conducted to date. Prolonged growth times are necessary to obtain large crystals. However, preliminary experiments in the present research revealed that growth ceased after a short period, and the crystals began to decompose.

This paper concerns our research regarding the growth of bulk GaN via vapor phase transport. We developed a high temperature nucleation technique to grow seed crystals and investigated processing windows for vertical and lateral growth to control the aspect ratio. We employed seeded growth to avoid multiple nucleation. We also studied the decomposition of GaN as a function of ammonia total pressure for continuous growth. Nitrogen dilution of ammonia has been investigated as a new and effective processing route for control of VPT growth of bulk GaN.

Experiment

Growth of GaN seed crystals and the seeded growth of bulk GaN using the former crystals were conducted in a dedicated system especially designed to achieve these objectives. The growth chamber consisted of a 4" diameter alumina reactor tube and a 16.5" outer stainless steel chamber that accommodated a dual graphite heater. The high temperature nucleation technique used to form the seed crystals consisted of heating the Ga(99.999%) source contained in a BN growth crucible and the substrate to 1260°C at ~ 20°C/min in nitrogen introduced from the top of the chamber, holding at this temperature for 20min, and then simultaneously switching the ambient gas from nitrogen to ammonia (in contrast to the conventional approach of introducing ammonia at room temperature at the outset of the experiment) and decreasing the substrate temperature to commence growth. The process variables of growth temperature, total ammonia pressure and ammonia flow rate were varied to obtain conditions for vertical and lateral growth. The vertical growth rate was calculated by dividing the length of each crystal along the c-direction by the growth time; the lateral growth rate was calculated by dividing half of the width of each crystal along the a-direction by the growth time. Needles and platelets with smooth surface morphologies were selected for seeded growth that was conducted under the conditions of 1130°C, 430Torr and 60sccm of ammonia or an ammonia/nitrogen mixture. The latter crystals were characterized using optical microscopy, scanning electron microscopy(SEM), Raman spectroscopy, and X-Ray diffraction(XRD).

Thin films of GaN grown by MOVPE were used in a decomposition study. The thickness and surface morphology of each film was determined after heating using cross-sectional SEM and atomic force microscopy(AFM), respectively. The composition of the gas phase was analyzed using quadruple mass spectrometry.

Results

The GaN seed crystals grown using the high temperature nucleation technique were larger relative to those grown by the conventional process at the same temperature, as shown in Figs. 1(a) and 1(b). This can be attributed to the reduced competition among nuclei for the incoming reactants due to the smaller number of nuclei that formed after the introduction of the ammonia at high temperature rather than at room temperature. This technique also produces, prior to nucleation, a clean substrate surface free of the liquid Ga, in contrast to the conventional nucleation process wherein observable amounts of Ga deposited on the substrate during ramp-up due to vigorous reaction between Ga and NH_3.

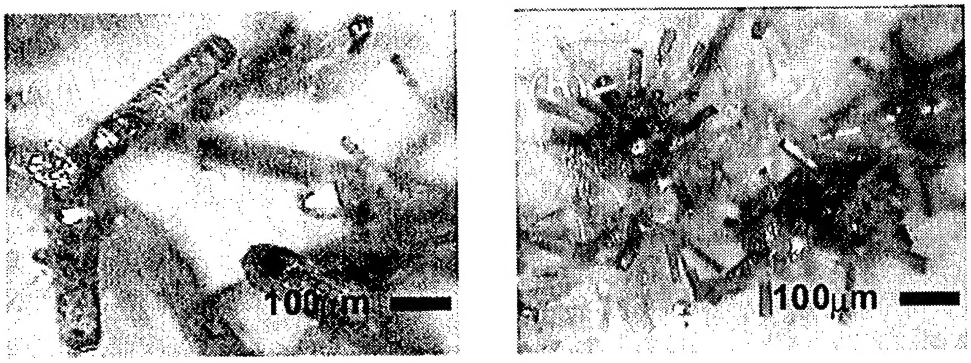

Figure 1. Optical micrographs of GaN crystals grown at 1130°C for 2hrs (a) by the high temperature nucleation technique and (b) by the conventional process.

Processing windows for vertical growth and lateral growth of the seed crystals at 1130°C were determined by constructing the three-dimensional plot shown in Fig. 2 of the aspect ratios of the GaN crystals versus the total pressure and the ammonia flow rate. The average lateral growth rate for the GaN platelets was ~50_m/hr; the average vertical growth rate for the needles was ~500_m/hr; growth rates in all other directions for these two morphologies were very low. Ammonia flow rates _75sccm and/or total pressures _430Torr and therefore lower V/III ratios favored lateral growth. Moreover, the use of flow rates >75sccm initiated the formation of GaN powder. The Ga flux increased with decreasing ammonia flow rate due to (1) reduced forced convection above the growing crystals and (2) with decreasing total pressure due to increased mean free path of Ga vapor. This was determined by growing GaN crystals using different Ga fluxes under otherwise identical growth conditions by placing a cover over the Ga source. Crystals grown with higher Ga fluxes (Fig. 3(a)) showed smooth surface morphology on the a-face and growth hillocks on the c-face. The different surface morphologies are due to different growth kinetics on different crystallographic planes. For the lower Ga fluxes, the lengths of the crystals did not change

appreciably, but the widths of the crystals decreased from ~85_m to ~15_m. This result supports the previous observation that a higher Ga flux promotes lateral growth[5]. Callahan, et al.[6] reported that GaN platelets were grown inside the Ga crust formed over the Ga melt where the Ga flux was higher. Both the a-face and the c-face of the crystals grown with the lower Ga flux were very rough (Fig. 3(b)), as the apparent result of decomposition. On the N-terminated surface under high V/III ratios, a nitrogen atom spontaneously bonds to a surface nitrogen atom to form a nitrogen molecule and a vacancy on the surface. The N_2 molecule is weakly bound and evaporates at elevated temperatures[7].

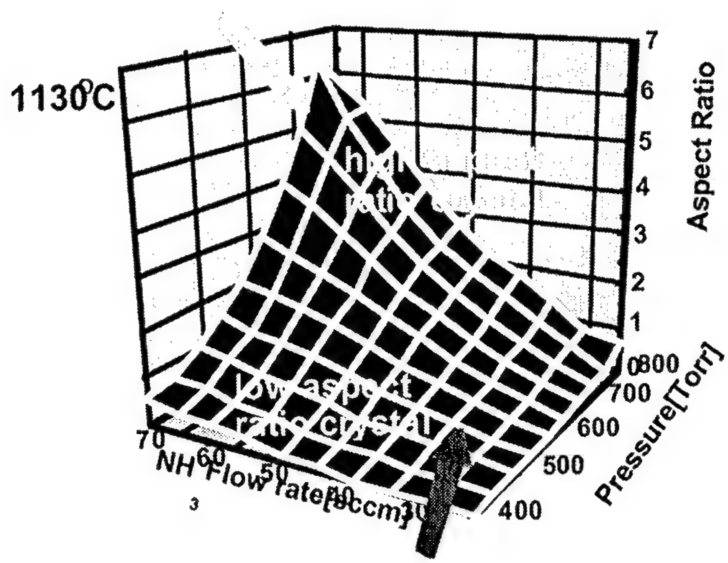

Figure 2. 3D plot of the aspect ratio of GaN crystals grown at 1130°C as a function of NH_3 flow rate and the total pressure.

Seeded growth was conducted on carefully selected GaN needles and platelets grown using the high temperature nucleation technique. No secondary nucleation was observed on the seed crystals (Figs. 4(a), 5(b)), while numerous randomly oriented GaN platelets were formed on the BN surface, as shown in Fig. 4(b). Surface morphologies of the GaN crystals were smooth (Figs. 4(c) and Fig. 5(b)). Raman spectra showed only the allowed modes of the wurtzite structure (Figs. 4(d) and Fig. 5(d)). Under the conditions of 1130°C, 430Torr, and 60sccm of NH_3, both the GaN needle(Fig. 4) and platelet seed crystals (Fig. 5) grew laterally at ~25_m/hr. A lower growth(<10_m/hr) was determined for the c-direction. The surface of the GaN platelet after seeded growth was partly covered by small powder-like GaN particles in a swirling pattern, as shown in Fig. 5(c). This appears to be a

post-growth feature that may have formed during cool-down, as the excess free Ga on the c-face reacts with ammonia at a lower temperature to form power-like GaN that is weakly bonded to the surface.

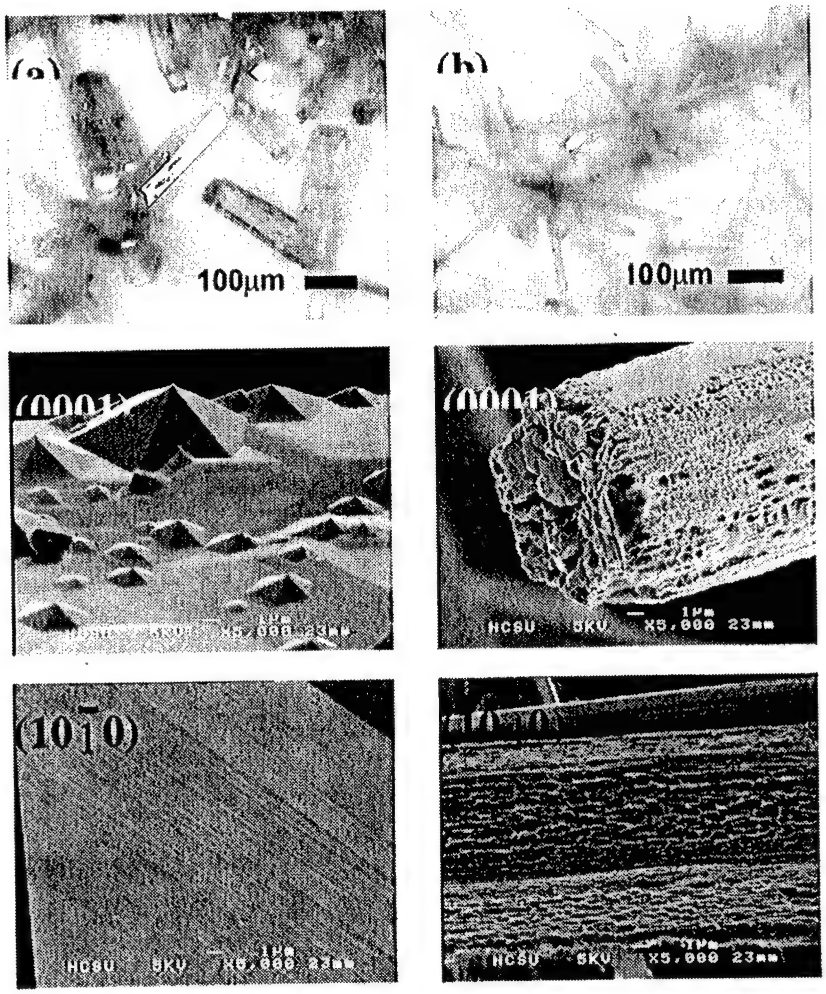

Figure 3. GaN crystals grown at 1130°C, 430Torr for 2hrs (a)without cover(higher Ga flux) (b)with cover (lower Ga flux) over the Ga source.

To produce larger crystals, prolonged growth is necessary. However, growth longer than 10 hours at 1130°C and 430Torr usually resulted in white crystals as a consequence of decomposition. The decomposition rate of GaN thin films was measured as a function of ammonia total pressure. The results are shown in Fig. 6. A minimum in the decomposition of GaN occurred between 430 and 510Torr at 1130°C; however, the error in each measurement disallowed the determination of the exact pressure. Mass spectroscopy revealed that the hydrogen concentration increased and the ammonia concentration decreased with increasing total pressure higher than 475Torr, as shown in Fig. 7.

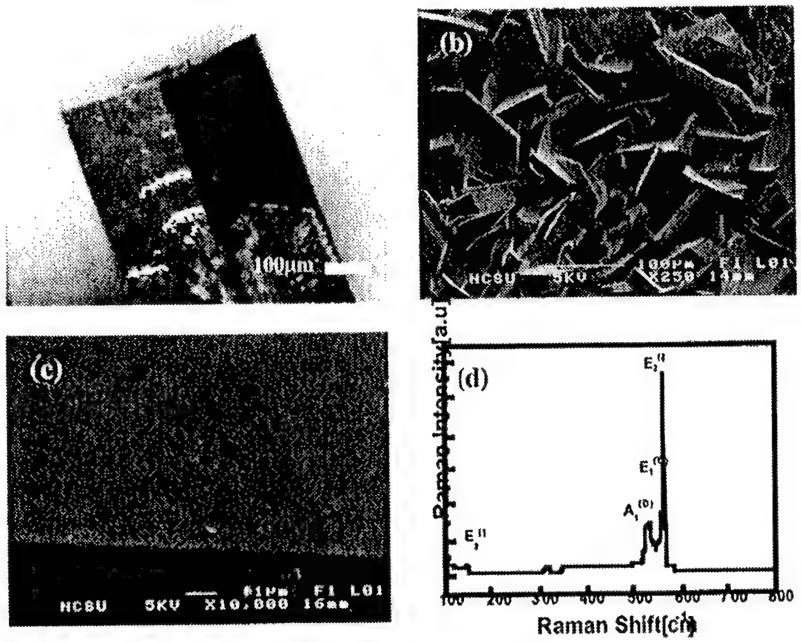

Figure 4 A GaN needle grown by seeded growth at 1130°C for 6hrs. (a) A needle after growth, (b) crystals grown on BN, (c) SEM micrograph of the c-face of the needle, and (d) Raman spectrum of the needle in (a).

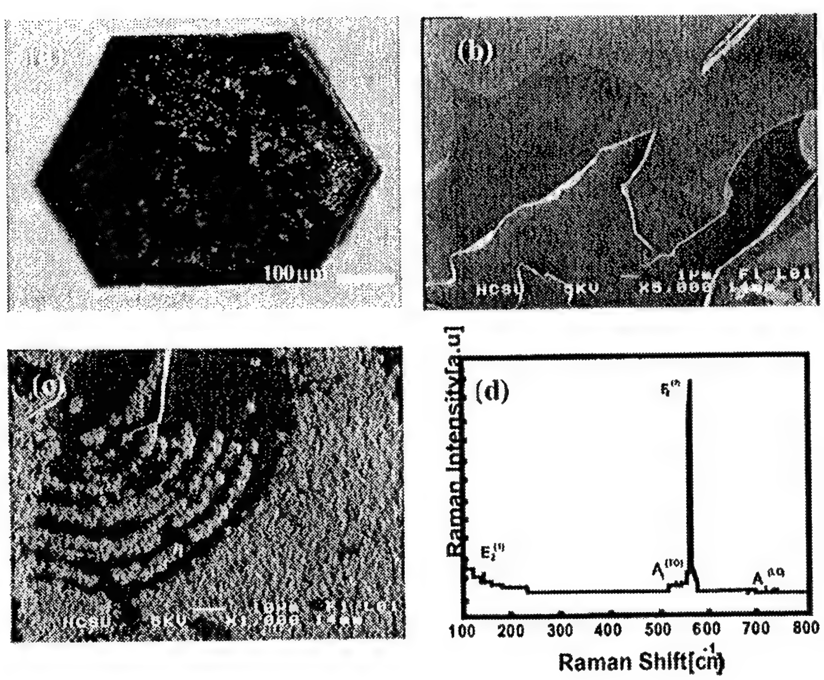

Figure 5. A GaN platelet grown by seeded growth at 1130°C for 6hrs. (a) the platelet after growth, (b) after growth,(c) Raman spectrum, (b) smooth area, and (c) rough area of the platelet

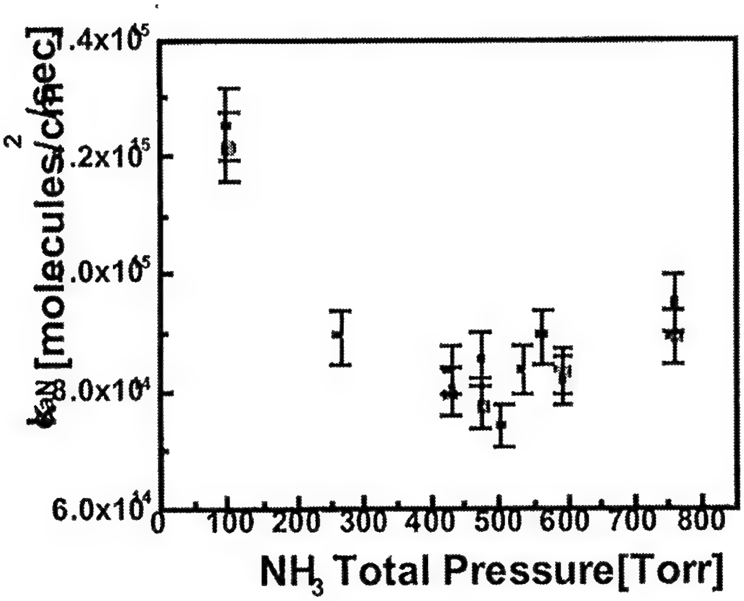

Figure 6. Decomposition rate of GaN at 1130°C and different ammonia total pressure.

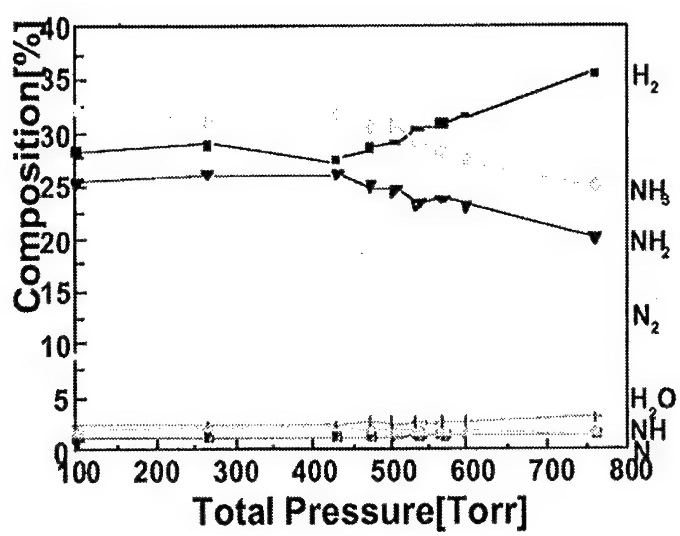

Figure 7. Composition of the Gas phase at 1130°C and different ammonia pressure.

This may be due to the increased number of collisions in the gas phase that increases the temperature and the consequent dissociation of ammonia molecules. Since hydrogen is a well-known etchant for GaN[8], this gas is responsible for the enhanced decomposition above 510Torr and especially at 760Torr. AFM images (Fig. 8) of the GaN (0001) surface

showed that it became roughest at 760Torr as a result of enhanced decomposition and smoothest at 100Torr due to enhanced desorption. Thus to achieve continued growth of the initial crystals, one must determine the process conditions that produce the desired compromise between thermodynamic instability and evaporation at low total pressures and decomposition due to hydrogen etching as a result of the decomposition of ammonia at high total pressures.

Based upon these results, ammonia was subsequently diluted with nitrogen in an effort to reduce the concentration of hydrogen as a byproduct of the dissociation of ammonia. A 2mm x 1.5mm GaN crystal was grown at 1130°C and 430Torr for 36hrs in a 66.7%NH_3+33.3%N_2 mixture with minimal decomposition, as shown in Fig. 9(a). A well-developed c-face and an a-face of the crystal, indicated by XRD patterns in Fig. 9(b) and (c), showed smooth surface morphologies, which are indicative of suppressed decomposition under the aforementioned growth conditions. The excellent crystallinity was confirmed by the FWHM of ~3cm^{-1} of the Raman $E_2^{(2)}$ mode(Fig. 9(d)).

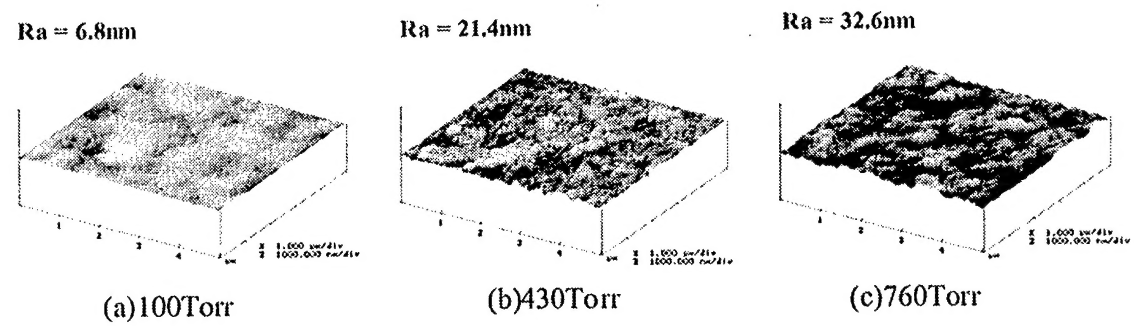

Figure 8. AFM images of the GaN surfaces after the heat treatment at 1130°C, 60sccm of NH_3 and total pressure of (a)100Torr, (b)430Torr and (c)760Torr.

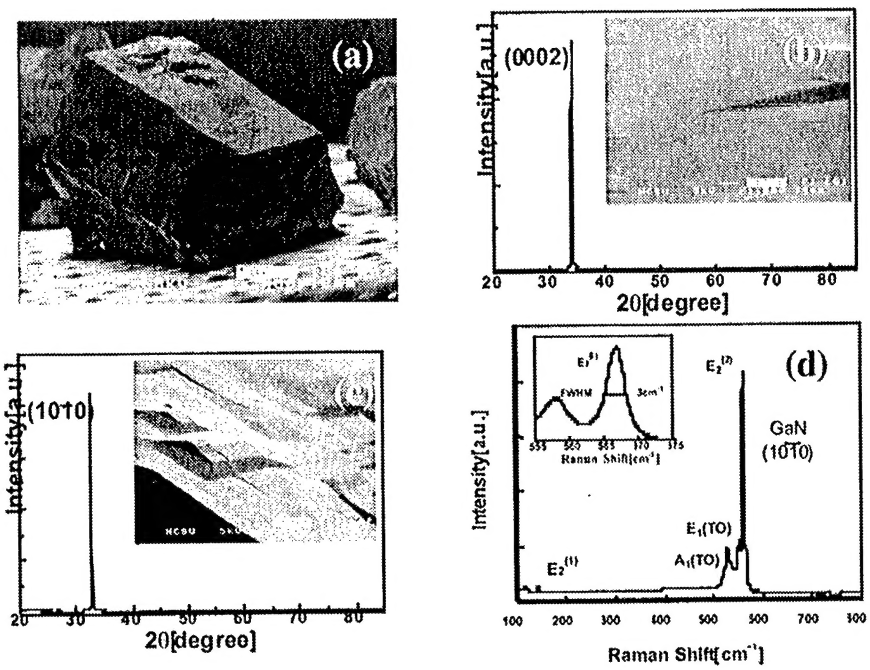

Figure 9. (a)SEM micrographs of the GaN crystal grown by seeded growth at 1130°C, 430Torr in 66.7%NH_3 +33.3%N_2 mixture for 36hrs, (b) XRD pattern of the c-face, (c) XRD pattern and (d) Raman spectrum of the a-face.

Conclusions

GaN seed crystals grown using a novel nucleation technique wherein NH_3 was introduced at high temperatures were larger than those grown by conventional growth process. Low V/III ratios, achieved using ammonia flow rates $\leq$ 75sccm and/or total ammonia pressures $\leq$ 430Torr, promoted lateral growth of GaN at 1130°C. Large needles and platelets of GaN crystals were grown by seeded growth without secondary nucleation. Evaporation at low total pressures and etching by hydrogen derived from the decomposition of ammonia at pressures higher than ~510Torr caused the cessation of growth of the seeded GaN crystals after ~10hrs. Nitrogen dilution of the NH_3 suppressed the high-pressure decomposition and allowed continuous growth of the seed crystals in contrast to those grown in pure ammonia. A 2mm x 1.5mm crystal was achieved using a 66.7%NH_3 and 33.3%N_2 gas mixture.

Acknowledgments

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